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(Statement A)

**In-Situ Oxygen-Atom Erosion Study of a Polyhedral
Oligomeric Silsesquioxane (POSS)-Siloxane Copolymer
Using a Novel Hyperthermal Oxygen Atom Source and
Analysis by X-ray Photoelectron Spectroscopy**

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ABSTRACT

The surface of a film of a polyhedral oligomeric silsesquioxane (POSS)-siloxane copolymer has been characterized in-situ using X-ray photoelectron spectroscopy (XPS) before and after exposure to incremental fluences of oxygen atoms produced by a novel hyperthermal oxygen atom source. The data indicate that the atomic oxygen initially attacks the cyclohexyl groups that surround the POSS cage resulting in the formation and desorption of CO_2 from the surface. The carbon concentration in the near surface region is reduced from 64.1 at% for the as-entered surface to 13.5 at% following 63 hrs^e of O-atom exposure at a flux of 10^{14} O-atoms/cm²-s. The oxygen and silicon concentrations are increased with incremental exposures to the O-atom flux but the rates of increase slow with increased exposure. The oxygen concentration increases from 18.1 at% for the as-entered sample to 54.0 at% following the 63 hr exposure, and the silicon concentration increases from 17.8 to 32.5 at% after 63 hrs^e. The data reveal the formation of a silica layer on the surface which serves as a protective barrier preventing further degradation of the polymer underneath with increased exposure to the O-atom flux.

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INTRODUCTION

The aggressive conditions present in low Earth orbit (LEO) at altitudes ranging from 200 to 700 km in the ionosphere reduce the longevity of organic materials used in the construction of space vehicles, thereby restricting the number of space-certified materials. The predominant environmental species in LEO responsible for this material degradation is atomic oxygen (AO) (1-4). AO is formed by the dissociation of molecular oxygen by ultraviolet radiation from the sun, resulting in a¹ AO concentration of approximately 10^8 atoms/cm³. The reverse reaction in which an oxygen molecule forms from AO does not have a high reaction rate because it requires a teratomic collision. The third O atom is required to carry away the energy released by formation of O₂. For this reason the predominant species in LEO is AO. The actual flux of $\sim 10^{15}$ atoms/cm²-s impinging on a spacecraft is high due to orbiting speeds of approximately 8 km/s. At these relative speeds AO particles collide with a kinetic energy of ~ 5 eV (5-8). The effect of AO on spacecraft material degradation has been studied on space exposed materials [STS missions and NASA Long Duration Exposure Facility (LDEF)] (9-11) and in simulation facilities (12-14). In these studies the samples were analyzed by X-ray photoelectron spectroscopy (XPS) but only after exposing the AO-treated samples to air. Recent studies have shown that exposure to air chemically alters the reactive surfaces formed during AO exposure (15,16). Therefore, in-situ AO erosion studies of polymers must be performed to avoid artifacts induced by air exposure.

In this study a thin film of polyhedral oligomeric silsesquioxane (POSS)-siloxane copolymer has been characterized in-situ using XPS before and after incremental exposures to the flux produced by a novel electron stimulated desorption (ESD) atomic oxygen source (17). POSS molecules are hybrid inorganic/organic structures synthesized from the self-condensation reactions of alkyl-trichlorosilanes. Over the last seven years, Lichtenhan ^{et al.} ~~and coworkers~~ have focused on incorporating POSS frameworks into traditional polymer systems via copolymerization, grafting and blending processes. (18)

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Significant property enhancements ~~have been reported~~ for these hybrid polymers including increased use temperature, increased toughness, decreased flammability and increased oxidation resistance (18). These property enhancements are attributed to the nano-level interaction of the POSS framework with the polymer matrix. Traditionally, silica fillers have been used in polymer applications requiring alterations in physical and mechanical properties such as tensile strength, abrasion and fatigue resistance. In addition to numerous property enhancements, POSS polymers are lighter weight (~ 1.2 to 1.5 g/ml) while silica fillers have much higher densities (~ 2.4 ^{to} 2.6 g/ml) (19). Unlike silica fillers, POSS frameworks can be easily functionalized for polymer compatibility without significantly affecting processing conditions. Compared to silica fillers, POSS hybrid polymers are able to impart similar property enhancements, including many not possible utilizing filler technology. Previous studies have also shown that Si-O systems exhibit a superior resistance to AO degradation due in part to their oxophilicity and high bond strength (~ 8 eV) (20). However, pure siloxane systems have displayed many disadvantages for space applications, including the generation of volatile cyclic species when exposed to AO that can recondense on optical surfaces (21). This present study details the results obtained from exposing a POSS-polydimethylsiloxane (PDMS) film to a simulated LEO environment. Specifically, it describes the formation of a protective silica layer with exposure to an O-atom flux. This layer serves as a protective barrier preventing further degradation of the underlying polymer with increased AO exposure.

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O-Atom Source Characteristics

The ESD source used in this study (Model OA10, Atom Sources, Inc.) is ultrahigh vacuum (UHV) compatible, operates with the sample at room temperature and produces a high-purity, hyperthermal, O-atom flux greater than 10^{15} atoms $\text{cm}^{-2} \text{s}^{-1}$ at a distance of 5 cm from the sample surface with an O atom: O^+ ratio of about 10^8 . These sources are superior to plasma sources in that they produce hyperthermal, ground-state O

atoms and operate at UHV pressures ($\sim 10^{-9}$ torr) with negligible amounts of other species, including contaminants and UV radiation. Because of the high reactivity of atoms, this O-atom source and a similar H-atom source have been used in numerous surface studies (22-27). The operational concept of the hyperthermal oxygen atom generator is shown in Fig. 1. Ultrahigh purity molecular O_2 dissociatively adsorbs on a metallic Ag alloy membrane at the high-pressure side and permeates at elevated temperature ($\sim 400^\circ\text{C}$) to the UHV side. There the adsorbed atoms are struck by a directed flux of primary electrons, which results in ESD of O atoms forming a continuous flux. Many processes have to function in series at sufficiently high rates for the system to work, including dissociative adsorption of the molecular gas on the metal surface, permeation of atoms through the membrane, and formation of the neutral flux by ESD. Based on the measured ion energy distribution and mass spectrometric experiments, the neutral energy distribution is believed to have a maximum at about 5 eV with a full width at half maximum of about 3.6 eV (28).

EXPERIMENTAL

Preparation of the POSS-PDMS copolymer

The POSS siloxane copolymer used in this study shown in Fig. 2a was synthesized using a method similar to that described by Lichtenhan et al. (29-30). ^{Five} 5.00 g (4.54 mmol) of the diol-silsesquioxane monomer shown in Fig. 2b was dissolved in 10 ml of THF in a 50-ml flask to which 1.98 g (4.54 mmol) of bis(dimethylamino)polydimethylsiloxane (approximately 4.9 silanes per oligomer, $M_w=435.5$ g/mol) was added with an additional 15 ml of THF. The reaction was stirred and heated to 65°C under nitrogen for 48 hrs. The polymer was then precipitated into 350 ml of methanol, stirred for 2 hrs, filtered and air dried for 12 hrs. To end cap the polymer with trimethylsilane, it was dissolved in 25 ml of THF with an excess of N,N -

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(dimethylamino)trimethylsilane and reacted at 65°C under nitrogen for another 48 hrs. The polymer was again precipitated into 350 ml of methanol. After decanting the solvent, fresh methanol with dilute HCl was added to neutralize any excess amine. The solution was again decanted and the remaining white solid ^{was} dried under vacuum for 2 hrs, producing a yield of 6.27 g (95% theoretical yield). Molecular weights were determined from multi-angle laser light scattering measurements obtained from a DAWN-F detector (Wyatt Technologies) equipped with a GPC column, $M_n = 62,000$, $M_w = 118,000$, degree of polymerization = 43. Analysis of the ^{29}Si NMR data gives a degree of polymerization of 38 and shows on average 4.8 SiOMe₂ groups per repeat unit. ^{29}Si NMR 7.2 ppm (singlet, Me₃Si -endgroups, 2.0) – 21.5 ppm (multiplet, Me₂Si-O, 184) – 66.39, - 68.13, - 68.20, -69.51 ppm (4 singlets, POSS, 305.6).

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Preparation of thin films by solvent casting

Thin films of the trimethylsilane terminated PDMS POSS were made by dissolving 100 mg of the coarse powder in 15-20 mL of THF, solvent casting onto 1 cm x 1 cm aluminum substrates and drying at room temperature for 24 hrs. The aluminum substrates were prepared and cleaned with soap and water, DI water followed by ultrasonic cleaning in acetone, trichloroethylene, acetone and ethanol respectively.

Surface Characterization

A solvent casted PDMS-POSS film was wiped with isopropanol and inserted into the UHV chamber (base pressure $<10^{-10}$ torr). XPS was performed using a double-pass cylindrical mirror analyzer (DPCMA) (PHI Model 25-270AR). XPS survey spectra were taken in the retarding mode with a pass energy of 50 eV, and high-resolution XPS spectra were taken with a pass energy of 25 eV using Mg K α X-rays (PHI Model 04-151 x-ray source). Data collection was accomplished using a computer interfaced, digital pulse-counting circuit (31) followed by smoothing with digital-filtering techniques (32).

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The sample was tilted 30 deg off the axis of the DPCMA, and the DPCMA accepted electrons emitted into a cone 42.6 6 deg off the DPCMA axis.

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XPS spectra were first obtained from the as-entered, solvent-cleaned sample. The sample was then transferred into an adjoining UHV chamber that houses the ESD O-atom source via a magnetically coupled rotary/linear manipulator. There the surface was exposed to a hyperthermal O flux and re-examined without air exposure after total exposure times of 2 hrs, 24.6 hrs, and 63 hrs. The approximate normal distance between the sample face and source in this study was 15 cm, at which distance the flux was about 2.0×10^{13} atoms/cm²-s for the instrument settings used. The sample was maintained at room temperature during the atom exposures with a slight temperature increase to 50°C due to exposure to the X-ray source during XPS data collection. The substrate temperature was determined using a chrome-alumel thermocouple. After the 63-hr AO exposure, the sample was exposed to air (room temperature, ~22°C, relative humidity ~60%) for 4.75 hrs and again examined using XPS.

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RESULTS AND DISCUSSION

XPS survey spectra obtained from an as-received, solvent-wiped POSS-PDMS surface before and after the 2, 24.6 and 63-hr O-atom exposure are shown in Fig. 3a to 3d, respectively. Spectrum e in Fig. 3 was taken after the 4.75-hr air exposure following the 63-hr O-atom treatment. The peak assignments shown in Fig. 4 pertain to all five spectra. The predominant peaks apparent in these spectra include the C 1s, O 1s, Si 2p, Si 2s, O 2s and O Auger peaks. Significant changes in relative peak heights are observed for the C, O, and Si features following the O-atom exposures. An estimate of the near surface composition has been calculated from the peak heights in the survey spectra by assuming that this region is homogeneous and using published atomic sensitivity factors (33). The compositions determined in this manner are presented in Table 1 for the as-entered, O-exposed and air exposed surfaces. The O 1s-to-Si 2p atomic ratio is 1.01 for

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the as-entered sample, and it is increased to 1.84 and then reduced to 1.66 and remains at 1.66 after the 2-, 24.6- and 63-hr O-atom exposures, respectively. After the 4.75-hr air exposure, the O 1s-to-Si 2p atomic ratio increases to 2.00. These increases in the O 1s-to-Si 2p atomic ratio resulting from exposure to the O-atom flux is characteristic of the formation of SiO_2 and is consistent with the high resolution spectra that follow. A significant reduction in the C 1s peak is observed as a result of the incremental exposures to the O-atom flux. The near-surface C concentration decreases from 64.1 at% for the as-entered sample to 13.5 at% after the 63-hr exposure. This decrease in C is due to the reaction of C in the near-surface region with O to form CO_2 . A slight increase in the carbon contribution to 18.1 at% is observed after exposing to air for 4.75 hrs probably due to the adsorption of C-containing molecules from the air. Hydrogen in the POSS would also react with the AO to form water which would desorb.

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High-resolution XPS C 1s, O 1s and Si 2p obtained from the as-received, solvent-wiped surface before and after the 2-, 24- and 63-hr O-atom exposures are shown in spectra a-d of Figs. 4, 5 and 6 respectively. Spectrum e was obtained after the 4.75-hr air exposure following the 63 hr O-atom exposure. Variations in peak shapes and positions are observed between the nonexposed, O-atom-exposed, and air-exposed surfaces, indicating that the chemical species distribution is altered by exposure to the O-atom flux and then to air.

The C 1s peak shown in Fig. 4a, is centered at 285.2 eV indicating that the predominant form of carbon present for the as-entered sample is in the form of a fully substituted hydrocarbon, i.e. the cyclohexyl groups on the POSS cage. (34) In spectra b-d, the C 1s peak becomes broader and the peak center shifts to lower binding energy (BE) with increasing exposure to the O-atom flux. After the 63-hr exposure, the C 1s has a BE of 284.4 eV. This value is characteristic of methyl groups on the PDMS chain (34). The fact that these changes coincide with a decrease in the total carbon concentration in the near surface region from 64.1 to 13.5 at% implies that the cyclohexyl groups are being

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removed selectively and leaving the methyl groups. This is due to the relative size of the POSS cage (1.5 nm) compared to the PDMS chain as shown in ^{Fig.} figure 2. Small shoulders are visible on the high BE side of the C 1s peak in spectra b, c and d. These probably are due to species such as alcohols, formaldehydes (BE ~286.0 to 287.7 eV) and organic acids (BE ~287.5) which form by reaction with the O-atom flux. Exposure to air (spectrum e) produces an increase in the shoulder near 285.0 eV. The O-atom exposure results in reactive surface sites which apparently adsorb hydrocarbons from the air. This observation is consistent with an increase in the C concentration after the air exposure as shown in Table 1.

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The O 1s spectra obtained from the sample after the various treatments are shown in Fig. 5. These peaks are broad indicating that various chemical states of oxygen are present. After the 2^{hr} exposure to the O-atom flux, the contribution from oxygen is significantly increased from 18.1 to 38.0 at%, and then increases further to 47.6 and 54.0 at% after the 24^{hr} and 63^{hr} exposures respectively. However, the peak shapes and positions do not change much with treatment indicating that the O-containing species have closely spaced O 1s BEs. A previous XPS study of PDMS has shown that the oxygen in the PDMS chain has a BE of 532.0 eV (34) while SiO₂ has a BE of between 532.5 eV. (35)

The Si 2p peaks obtained from the sample after the various treatments are shown in Fig. 6. Similar to the O 1s peak, the Si 2p peak for the as-entered sample (spectrum a) is broad[^] indicating the presence of several chemical states of silicon. This peak is centered at a BE of 102.7 eV which corresponds to RSiO_{1.5} in the POSS cage. However, spectra b, c and d reveal the formation of a SiO₂ layer with incremental exposures to the O-atom flux. The fact that little difference is observed in the spectra obtained after the 24-hr and 63-hr exposures indicates that this silica layer forms a protective barrier on the surface which prevents further degradation of the polymer with longer exposure to the O-atom flux. The 5-eV AO is not energetic enough to penetrate more than one or two

atomic layers into the polymer while XPS probes as deeply as 30 or more atomic layers beneath the surface. The significant compositional changes observed indicate that most of the near-surface region examined by XPS is altered by the AO exposure. The chemical reactions which form CO_2 and H_2O are exothermic so the local surface temperature may be relatively high. This ~~fact~~^{fact} and the fact that the AO induces a chemically induced driving force result in diffusion of subsurface C and H to the surface where they react with the AO. This mechanism is responsible for the subsurface compositional alterations observed using XPS.

CONCLUSION

The surface of a film of a polyhedral oligomeric silsesquioxane-siloxane copolymer has been characterized in-situ using XPS before and after exposure to different fluences of oxygen atoms produced by a novel hyperthermal oxygen atom source.

The XPS data indicate that exposure to the O-atom flux reduces the carbon content on the surface from 64.1 to 13.5 at% after a 63-hr exposure to an O-atom flux of 10^{14} atoms/cm².

s. The oxygen and silicon concentrations in the near-surface region determined using XPS increases with increasing exposure to the O flux. The oxygen-to-silicon ratio increases from 1.01 for the as-entered sample to 1.66 after 63 hrs of O-atom exposure; and after exposure to air this ratio increases to 2.00. High resolution XPS data suggest that the atomic oxygen initially attacks the cyclohexyl groups on the POSS cage forming CO_2 which desorbs. Increased exposure to the O-atom flux results in the formation of a silica layer on the surface which acts a protective barrier preventing further degradation of the underlying polymer. Exposure to air results in the adsorption of hydrocarbon species on the surface.

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ACKNOWLEDGMENT

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Table 1 Near-surface composition determined from XPS data obtained from the as-entered, solvent cleaned, O-atom and air-exposed POSS-PDMS sample

Surface	Composition, at%		
Sample Treatment	O	C	Si
As entered, solvent cleaned	18.1	64.1	17.8
2-h O-atom exposure	38.0	41.3	20.7
24-h O-atom exposure	47.6	23.7	28.6
63-h O-atom exposure	54.0	13.5	32.5
4.75-h air exposure following 63-h O-atom exposure	54.6	18.1	27.3

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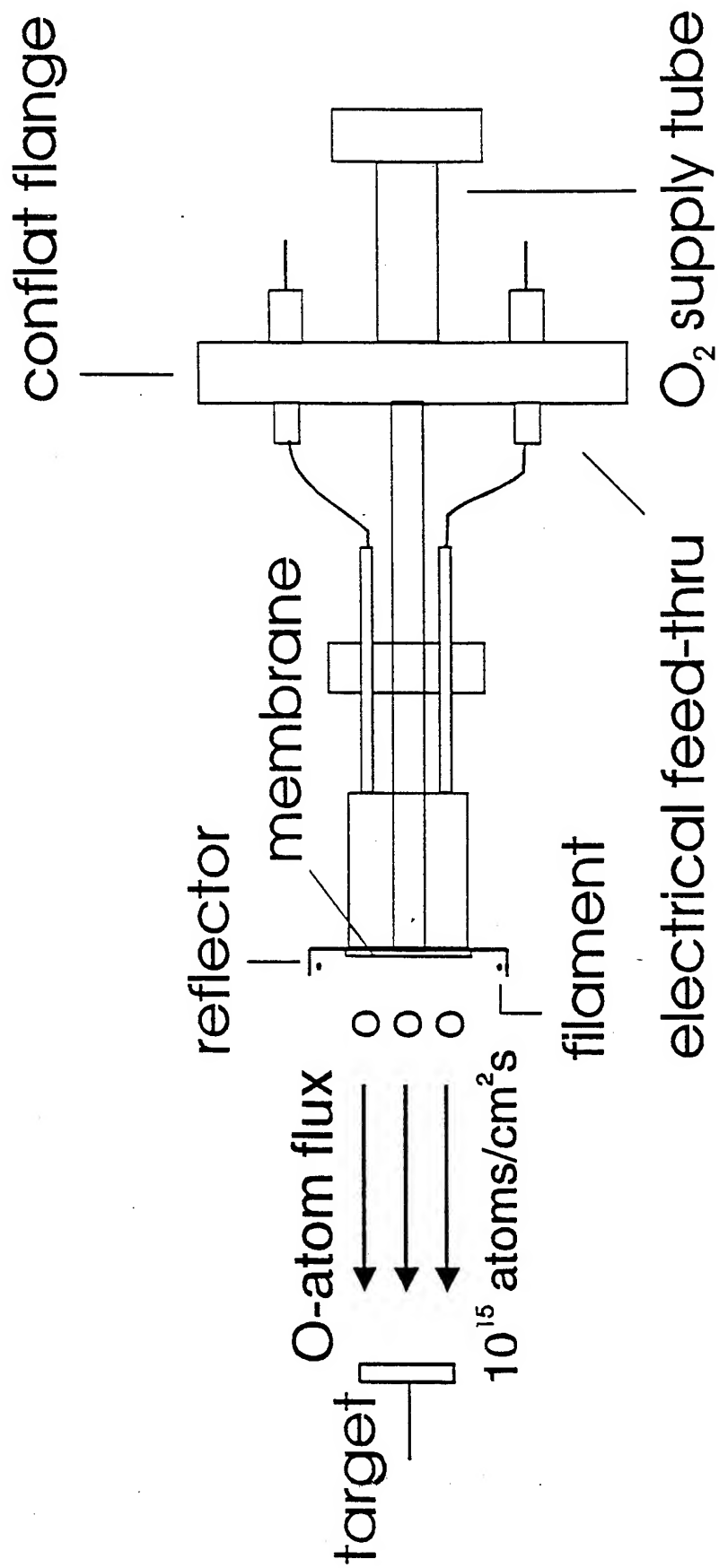


book
titles -
see previous
note

FIGURE CAPTIONS

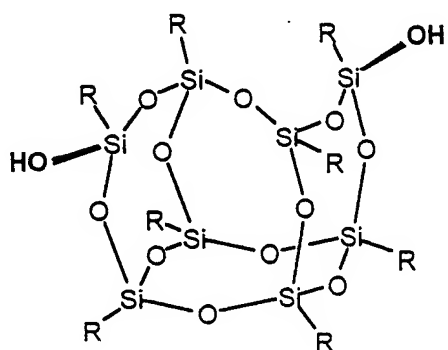
- Figure 1** Schematic diagram of the atom source.
- Figure 2** Synthetic scheme for synthesis of the POSS-PDMS (polydimethylsiloxane) copolymer used in this
- Figure 3** XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.75 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 4** XPS C 1s spectra obtained from a solvent-cleaned, POSS-PDMS film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.75 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 5** XPS O 1s spectra obtained from a solvent-cleaned, POSS-PDMS film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.75 hr air exposure following the 63 hr O-atom exposure (e).
- Figure 6** XPS Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film after insertion into the vacuum system (a), after 2 hr (b), 24 hr (c), and 63 hrs exposure to the hyperthermal O-atom flux (d), and 4.75 hr air exposure following the 63 hr O-atom exposure (e).

Where
are
these?

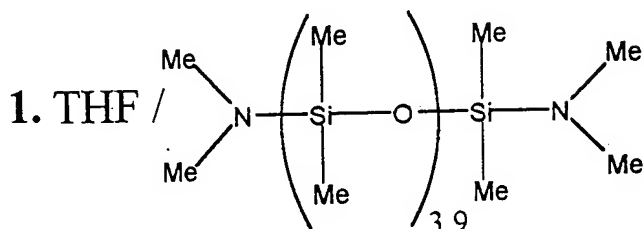


Need to include
figure numbers -
they are referred
to in text
that way

Fig 1?



R = cyclohexyl



2. Work up reaction in MeOH

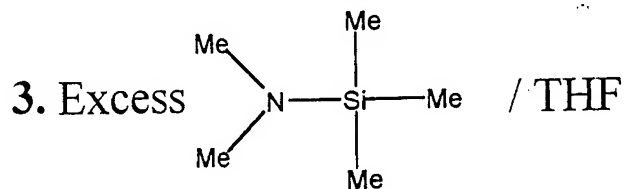


Fig 2a

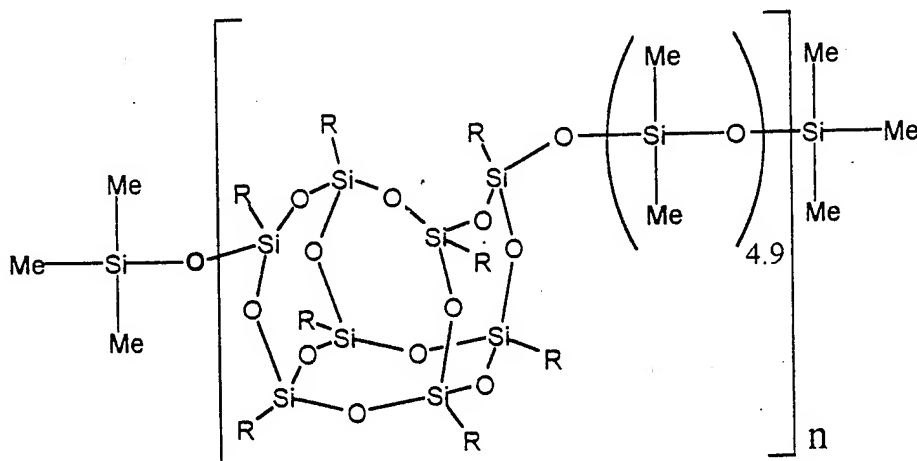
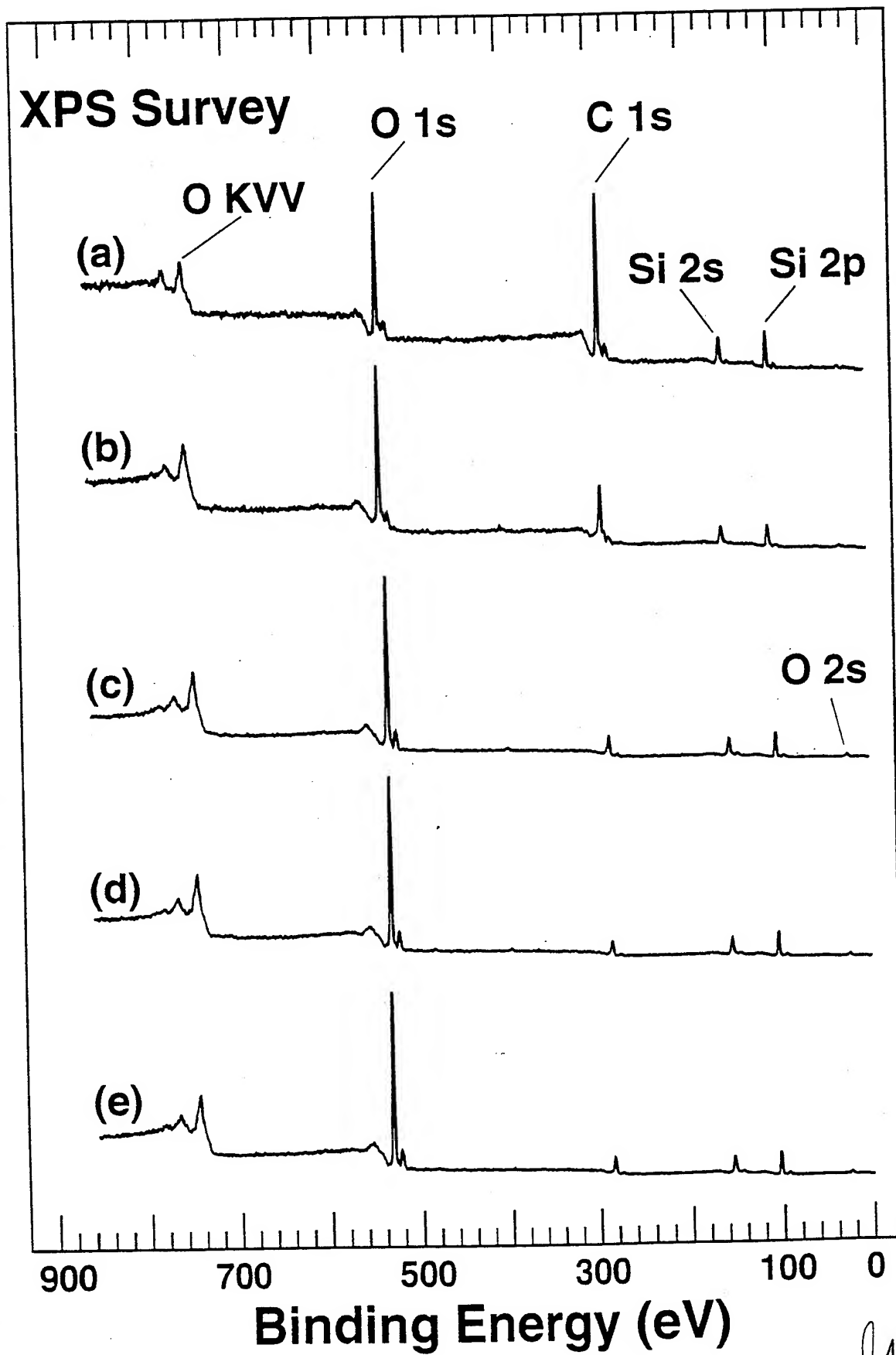
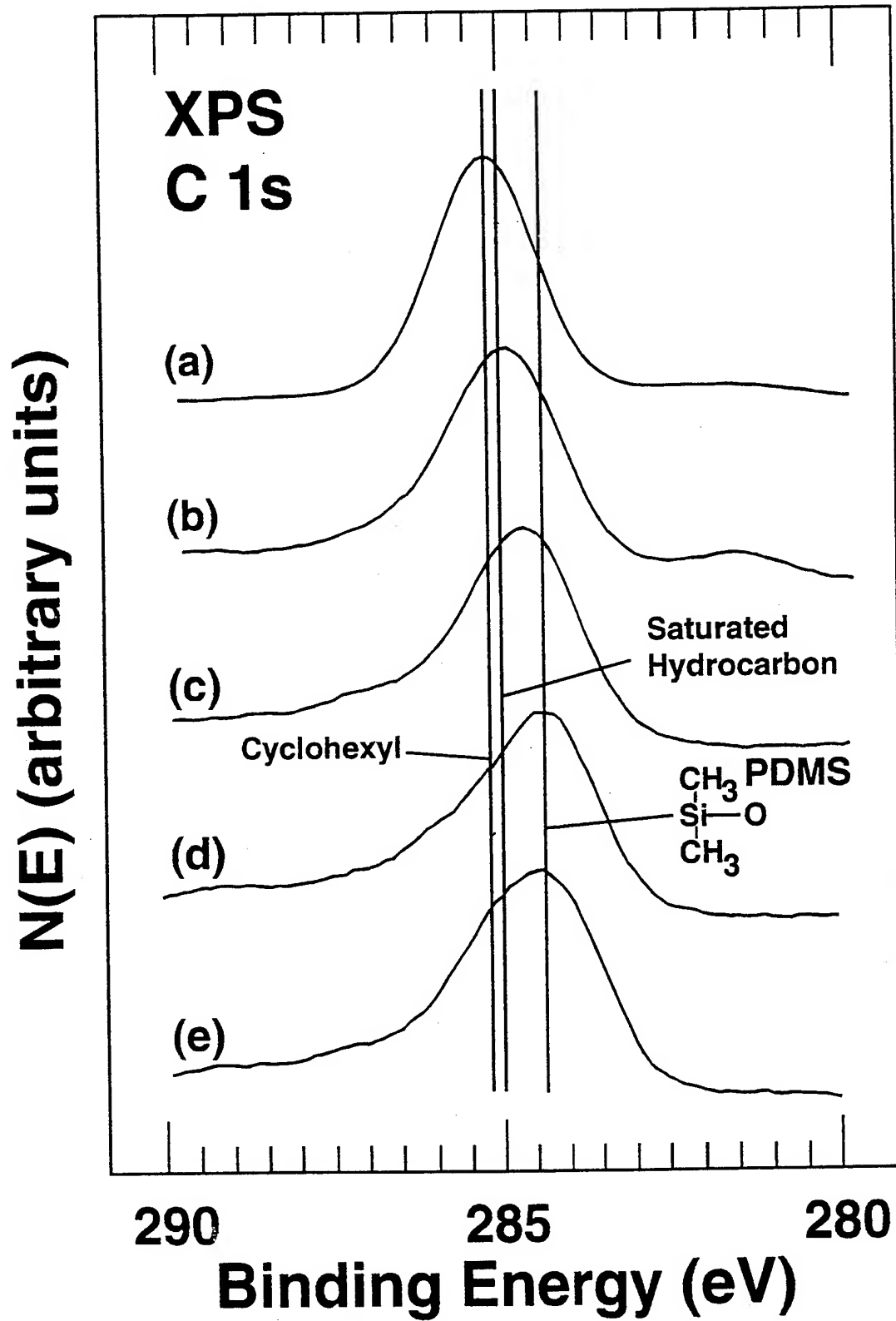


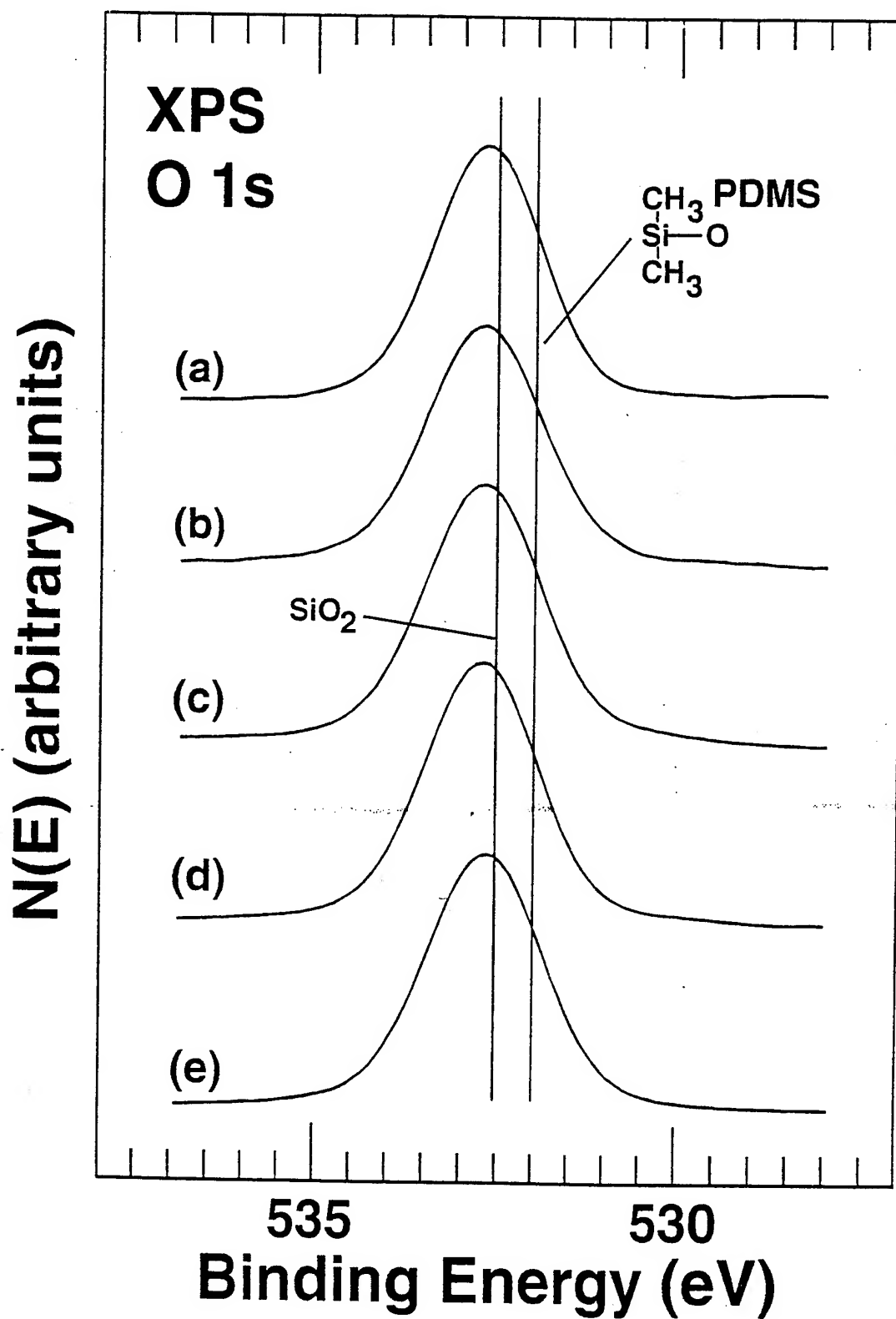
Fig 2b

N(E) (arbitrary units)



is this 3a





3c?

N(E) (arbitrary units)

XPS
Si 2p

(a)

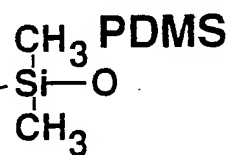
SiO₂

(b)

(c)

(d)

(e)



105 100
Binding Energy (eV)

3d?